

DECLARATION

- I, Itsuko KAJIWARA, a national of Japan,
 c/o Asamura Patent Office of 331-340, New Ohtemachi
 Building, 2-1, Ohtemachi-2-chome, Chiyoda-ku, Tokyo, Japan
 do hereby solemnly and sincerely declare:
- THAT I am well acquainted with the Japanese language and English language, and
- 2) THAT the attached is a full, true, accurate and faithful translation into the English language made by me of Japanese Patent Application No. 2003-004194.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 27th day of April , 2006

THOUSE KATTWARA



2003-004194

[Title of Document]

Patent Application

[Reference Number]

P155256

[Data of Submission]

January 10, 2003

[Addressee]

Commissioner

The Patent Office

[International Patent Classification]

C11D 7/06

H01L 21/304

[Inventor]

[Address]

c/o SUMITOMO CHEMICAL COMPANY, LIMITED,

6, Kitahara, Tsukuba-shi, Ibaraki,

Japan.

[Name]

Masayuki TAKASHIMA

[Inventor]

[Address]

c/o NEC Electronics Corporation,

1753, Shimonumabe, Nakahara-Ku,

Kawasaki-shi, Kanagawa, Japan.

[Name]

Yoshiko KASAMA

[Inventor]

[Address]

c/o NEC Electronics Corporation,

1753, Shimonumabe, Nakahara-Ku,

Kawasaki-shi, Kanagawa, Japan.

[Name]

Hiroaki TOMIMORI

[Inventor]

[Address]

c/o NEC Electronics Corporation,

1753, Shimonumabe, Nakahara-Ku,

Kawasaki-shi, Kanagawa, Japan.

[Name]

Hidemitsu AOKI

2003-004194

[Applicant]

[Applicant's ID Number] 0 0 0 0 0 2 0 9 3

[Name]

SUMITOMO CHEMICAL COMPANY, LIMITED

[Applicant]

[Applicant's ID Number] 3 0 2 0 6 2 9 3 1

[Name]

NEC Electronics Corporation

[Agent]

[Agent's ID Number]

1 0 0 0 9 3 2 8 5

[Patent Attorney]

[Name]

Takashi KUBOYAMA

[Telephone]

06-6220-3405

[Agent]

[Agent's ID Number]

1 0 0 1 1 3 0 0 0

[Patent Attorney]

[Name]

Toru NAKAYAMA

[Telephone]

06-6220-3405

[Agent]

[Agent's ID Number]

1 0 0 1 1 9 4 7 1

[Patent Attorney]

[Name]

Masayuki ENOMOTO

[Telephone]

06-6220-3405

2003-004194

[Indication on Fee]			
[Prepayment Register N	Number]	010238	
[Amount of Payment]		¥21,000-	
[List of Items Filed]			
[Title of Article]	Specifica	tion1	L
[Title of Article]	Drowings	1	L
[Title of Article]	Abstract		L
[Number of General Pow	ver]	0 2 1 2 9 4 9	
[Proof: Required or not]		Yes	

[Kind of Document] Description

[Title of the Invention] CLEANING SOLUTION FOR SEMICONDUCTOR SUBSTRATE

[Claims]

[Claim 1] A cleaning solution for semiconductor substrates which contains a nonionic surface active agent represented by the following formula (1), a chelating agent and a chelating accelerator:

$$CH_3 - (CH_2)_1 - O - (C_m H_{2m}O)_n - X$$
 (1)

(in the formula, 1, m and n independently represent a

10 positive number, and X represents a hydrogen atom or a
 hydrocarbon group).

[Claim 2] A cleaning solution according to claim 1, wherein 1 is 8-11.

[Claim 3] A cleaning solution according to claim 1, wherein m is 2 and n is 5-10.

[Claim 4] A cleaning solution according to any one of claims 1-3, wherein the chelating agent is at least one compound selected from the group consisting of polyaminocarboxylic acids, polycarboxylic acids,

compounds having phosphonic acid group, oxycarboxylic acids, phenols, heterocyclic compounds and tropolones.

[Claim 5] A cleaning solution according to any one of claims 1-4, wherein the chelating agent is at least one

compound selected from the group consisting of ethylenediaminetetraacetic acid, oxalic acid, ammonium oxalate, hydroxyethylidenediphosphonic acid, citric acid, ammonium citrate, catechol, 8-quinolinol, and tropolone.

[Claim 6] A cleaning solution according to any one of claims 1-5, wherein the chelating accelerator contains a hydroxide and a fluoride or a salt thereof.

[Claim 7] A cleaning solution according to claim 6,

wherein the hydroxide is a compound containing no metal.

[Claim 8] A cleaning solution according to claim 6 or

7, wherein the hydroxide is at least one compound

selected from the group consisting of ammonium

hydroxide, tetramethylammonium hydroxide and choline.

15 [Claim 9] A cleaning solution according to any one of claims 6-8 wherein the fluoride or salt thereof is hydrofluoric acid or ammonium fluoride.

20

25

molecule.

[Claim 10] A cleaning solution according to any one of claims 1-9 which further comprises a corrosion inhibitor for metals.

[Claim 11] A cleaning solution according to claim 10, wherein the corrosion inhibitor for metals contains an organic compound having at least one of nitrogen atom, oxygen atom, phosphor atom and sulfur atom in the

[Claim 12] A cleaning solution according to claim 10 or 11, wherein the corrosion inhibitor for metals contains a compound having at least one azole group in the

molecule.

[Claim 13] A cleaning solution according to any one of claims 10-12, wherein the corrosion inhibitor for metals contains an aliphatic alcohol compound having at least one mercapto group, the carbon atom to which the mercapto group is bonded and the carbon atom to which the hydroxyl group is bonded being adjacent to each other.

[Claim 14] A cleaning solution according to any one of claims 10-12 which has a pH of 7 or higher.

[Claim 15] A method for making a semiconductor device which comprises cleaning an insulating film of low dielectric constant exposed on the surface of a semiconductor substrate using the cleaning solution of

15 any one of claims 1-14

[Detailed Description of the Invention]
[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a cleaning solution for semiconductor substrates.

[0002]

[Prior Art]

Recently, Cu wiring is introduced into semiconductor devices, and for the formation of Cu

10 wiring, a chemical and mechanical polishing process (CMP process) is employed.

This CMP process comprises forming grooves or connecting holes in a previously flattened insulating film of low dielectric constant, such as of carbon-containing SiO₂ (SiOC), then forming a Cu film, for example, by plating method to fill the grooves or connecting holes, and polishing the surface with a slurry containing special abrasive grains and additives to remove Cu in the portions other than the grooves or connecting holes, thereby flattening the surface and forming the wiring or connecting holes.

On the semiconductor substrate after subjected to the CMP process, there are fine foreign particulate substances such as abrasive grains contained in the polishing slurry or polishing detritus and ionic foreign substances such as metal impurities in large amounts. Therefore, it has been demanded to develop cleaning solutions which can remove simultaneously the

particulate foreign substances and ionic foreign substances.

As these cleaning solutions, there have been known, for example, those which contain a nonionic

5 surface active agent such as polyoxyethylenenonylphenyl ether, a compound forming a complex with a metal such as aminoacetic acid or quinaldic acid, and an alkali component (Patent Document 1).

However, the above cleaning solutions are inferior in wettability with hydrophobic insulating films of low dielectric constant, such as of SiOC, and it is difficult to remove the particulate foreign substances and ionic foreign substances on the semiconductor substrates after subjected to CMP process.

15 [0003]

[Patent Document 1] JP-A-2002-270566

[0004]

[Problem to be solved by the Invention]

The object of the present invention is to provide a cleaning solution excellent in removability of particulate foreign substances and ionic foreign substances present on a semiconductor substrate after subjected to CMP process.

25 [0005]

[Means for solving Problem]

As a result of intensive research conducted by the inventors in an attempt to find a cleaning solution

which can solve the above problems, it has been found that a cleaning solution containing nonionic surface active agent having no phenylene group which is represented by the following formula (1), a chelating agent and a chelating accelerator is excellent in removal of particulate foreign substances and ionic foreign substances present on a semiconductor substrate. Thus, the present invention has been accomplished.

[0006]

That is, the present invention provides a cleaning solution for semiconductor substrates which contains a nonionic surface active agent represented by the following formula (1), a chelating agent and a chelating accelerator:

15

20

25

$$CH_3 - (CH_2)_1 - O - (\bar{C}_m H_{2m} O)_n - X$$
 (1)

(in the above formula, 1, m and n independently represent a positive number, and X represents a hydrogen atom or a hydrocarbon group).

[0007]

[Mode for Carrying Out the Invention]

The cleaning solution of the present invention comprises a nonionic surface active agent represented by the formula (1), a chelating agent and a chelating accelerator:

$$CH_3 - (CH_2)_1 - O - (C_m H_{2m}O)_n - X$$
 (1)

(in the above formula, 1, m and n independently represent a positive number, and X represents a hydrogen atom or a hydrocarbon group).

In the formulas (1), 1 represents a positive number and is preferably 8-18, more preferably 8-11, and further preferably 9-11.

If l is less than 8 or more than 18, the cleaning solution becomes inferior in wettability with an insulating film of low dielectric constant, and satisfactory removability of particulate foreign substances tends to decrease. Especially, if l exceeds 18, action as an oleophilic group increases and hence the nonionic surface active agent hardly dissolves in an aqueous solution.

[0008]

20

In the nonionic surface active agent represented the formula (1), it is preferred that the starting material is a primary alcohol, and 1 is 9 or 11.

Even if the total carbon numbers is 12, the nonionic surface active agent produced from a secondary alcohol represented by the following formulas (2) is insufficient in removability of particulate foreign although wettability with an insulations film of low dielectric constant.

$$(CH_3 - (CH_2)_{\ell})_2 CH - O - (C_m H_{2m}O)_n - X$$
 (2)

[0009]

[0010]

In the nonionic surface active agent (1), m represents a positive number and is preferably 2 or 3, 5 more preferably 2.

A surface active agent obtained by copolymerizing ethylene oxide of m being 2 and propylene oxide of m being 3 does not have satisfactory cleaning properties.

In the nonionic surface active agent (1), n represents a positive number and is preferably 4-20, more preferably 5-10.

If n is less than 4, dissolvability in the aqueous solution is inferior and if n is more than 20, wettability with an insulating film of low dielectric constant deteriorates.

Examples of the nonionic surface active agent represented the formulas (1) are polyoxyethylene decyl ether polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene polyoxypropylene lauryl ether, polyoxyethylene polyoxypropylene stearyl ether, etc.

Among them, polyoxyethylene decyl ether and polyoxyethylene lauryl ether are preferred.

[0011]

The concentration of the nonionic surface

active agent (1) in the cleaning solution is preferably 0.0001-1% by weight, more preferably 0.001-1% by weight.

If the concentration is less than 0.0001% by weight, wettability with an insulating film of low dielectric constant tends to deteriorate, and if it exceeds 1% by weight, the cleaning solution froths vigorously to hinder the operation of cleaning.

[0012]

The chelating agent is not particularly

limited so long as it can remove metals. As examples thereof, mention may be made of at least one compound selected from the group consisting of polyamino-carboxylic acids, polycarboxylic acids, compounds having phosphonic acid group, oxycarboxylic acids, phenols,

beterocyclic compounds and tropologies. They include

15 heterocyclic compounds and tropolones. They include salts or derivatives thereof.

The polyaminocarboxylic acids include, for example, ethylenediaminetetraacetic acid (EDTA), trans-1,2-cyclohexanediaminetetraacetic acid (CyDTA),

nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), and N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (EDTA-OH).

Among them, ethylenediaminetetraacetic acid (EDTA) is preferred.

25 [0013]

The polycarboxylic acids include, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, methylmalonic acid, 2-carboxybutyric acid, and ammonium

salts of these acids.

Among them, oxalic acid and ammonium oxalate are suitable.

[0014]

- The compounds having phosphonic acid group include, for example, ethylenediaminetetramethylene-phosphonic acid, ethylenediaminedimethylenephosphonic acid, nitrilotrismethylenephosphonic acid, and 1-hydroxyethylidenediphosphonic acid.
- Among them, 1-hydroxyethylidenediphosphonic acid is suitable.

[0015]

The oxycarboxylic acids include, for example, gluconic acid, tartaric acid and citric acid.

Among them, citric acid and ammonium citrate are suitable.

[0016]

The phenols include, for example, phenol, cresol, ethylphenol, t-butylphenol, methoxyphenol,

20 catechol, resorcinol, hydroquinone, 4methylpyrocatechol, 2-methylhydroquinone, pyrogallol,

3,4-dihydroxybenzoic acid, gallic acid, 2,3,4trihydroxybenzoic acid, 2,4-dihydroxy-6-methylbenzoic
acid, ethylenediaminediorthohydroxyphenylacetic acid

25 [EDDHA], N,N-bis(2-hydroxybenzyl)ethylenediamine-N,Ndiacetic acid [HBED], and ethylenediaminedihydroxymethylphenylacetic acid [EDDHMA].

Among them, catechol and

ethylenediaminediorthohydroxyphenylacetic acid [EDDHA] are suitable.

[0017]

The heterocyclic compounds include, for
example, 8-quinolinol, 2-methyl-8-quinolinol,
quinolinediol, 1-(2-pyridyl-azo)-2-naphthol, 2-amino4,6,7-pteridinetriol, 5,7,3',4'-tetrahydroxyflavone
[luteolin], 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]fluorescein [calcein], and 2,3-hydroxypyridine.

Among them, 8-quinolinol is suitable.

[0018]

The tropolones include, for example, tropolone and 6-isopropyltropolone.

Among them, tropolone is suitable.

15 [0019]

The concentration of the chelating agent in the cleaning solution is preferably 0.00001-10% by weight, more preferably 0.0001-1% by weight.

If the concentration is less than 0.00001% by
weight, performance for removing metals as chelating
agent tends to decrease, and if it exceeds 10% by
weight, solubility in the cleaning solution tends to
lower.

[0020]

25 The chelating accelerator is added for more effectively chelating the metal impurities deposited on the semiconductor substrates.

As the chelating accelerators, mention may be

made of general acidic compounds, alkaline compounds, salts thereof, organic compounds etc. They include preferably hydroxides and fluorides or salts thereof.

Those which contain only hydroxides or only fluorides or salts thereof cannot sufficiently exhibit the effects, and those which contain both of them can improve the metal removability with the chelating agents.

The hydroxides include, for example, inorganic compounds such as sodium hydroxide, potassium hydroxide and ammonium hydroxide; hydroxides of quaternary ammonium, such as tetramethylammonium hydroxide and choline; and alkanolamines such as monoethanolamine, diethanolamine, triethanolamine, 2-methylaminoethanol,

2-ethylaminoethanol, N-methyldiethanolamine, dimethylaminoethanol, 2-(2-aminoethoxy)ethanol, 1-amino-2-propanol, monopropanolamine, and dibutanolamine.

Among them, compounds containing no metal, such as ammonium hydroxide, tetramethylammonium hydroxide and choline can be suitably used from the viewpoint that they do not contaminate the surface of semiconductor substrate (silicon wafer) with metals.

20

The concentration of the hydroxide in the cleaning solution is preferably 0.0001-30% by weight,

25 more preferably 0.001-1% by weight. If the concentration is less than 0.0001% by weight, the metal removability tends to lower, and if it exceeds 30% by weight, film quality of the insulating film of low

dielectric constant tends to deteriorate.

[0021]

The fluorides or salts thereof include, for example, hydrofluoric acid, potassium fluoride, sodium fluoride and ammonium fluoride.

Among them, ammonium fluoride is suitable.

The concentration of the fluoride or salt thereof in the cleaning solution is preferably 0.0001-40% by weight, more preferably 0.01-5% by weight.

If the concentration is less than 0.0001% by weight, the metal removability tends to lower, and if it exceeds 40% by weight, quality of the insulating film of low dielectric constant tends to deteriorate while metal removability is not improved.

15 [0022]

As to the relation in concentration of the hydroxide and the fluoride or salt thereof, the concentration of the hydroxide is preferably lower than that of the fluoride or salt thereof.

If the concentration of the hydroxide is higher than that of the fluoride or salt thereof, quality of the under insulating film of low dielectric constant tends to deteriorate.

[0023]

The cleaning solution of the present invention aims at removing particulate foreign substances and ionic foreign substances on a semiconductor substrate (wafer) having exposed insulating film of low dielectric

constant during preparation of semiconductor devices, but since Cu wiring is also sometimes exposed, the cleaning solution of the present invention preferably further contains a corrosion inhibitor for metals.

The corrosion inhibitors for metals preferably have at least one of nitrogen atom, oxygen atom, phosphor atom and sulfur atom in the molecule, and more preferred are compounds having at least one azole group in the molecule, such as benzotriazole, tolutriazole, 4methylimidazole, 5-hydroxymethyl-4-methylimidazole and 10 3-aminotriazole.

It is further preferred that the corrosion inhibitors for metals contain an aliphatic alcohol compound of 2 or more carbon atoms which has at least 15 one mercapto group, the carbon atom to which the mercapto group is bonded and the carbon atom to which hydroxyl group is bonded being adjacent to each other.

Examples of the corrosion inhibitors for metals are thioglycerol and thioglycol.

20 [0024]

25

5

The pH of the cleaning solution of the present invention is preferably 7 or higher (alkaline). If the pH is lower than 7 (acidic), not only the removability for fine particles tends to deteriorate, but also corrosion due to battery effect between Cu and barrier metal is apt to occur during cleaning operation.

[0025]

The cleaning solution of the present invention

is excellent in removal of particulate foreign substances and ionic foreign substances on a semiconductor substrate (wafer), on the surface of which an insulating film of low dielectric constant is exposed.

As the insulating films of low dielectric constant, mention may be made of inorganic films such as of FSG (F-containing SiO₂), SiOC (carbon-containing SiO₂) and SiON (N-containing SiO₂), polyorganosiloxane films

10 such as of MSQ (methylsilsesquioxane), HSQ (hydrogensilsesquioxane) and MHSQ (methylated hydrogensilsesquioxane, aromatic films such as of PAE (polyaryl ether) and BCB (divinylsiloxane-bis-benzocyclobutene), and organic films such as of Silk and porous SilK, etc.

The insulating film of low dielectric constant in the present specification usually means an insulating film having a relative dielectric constant of not higher than 3.0.

20 The cleaning solutions of the present invention can be used irrespective of kind of the insulating films of low dielectric constant and method of the film formation, but since they are effective especially for the insulating films such as of SiOC, MSQ 25 and PAE (polyaryl ether), preferably they are used for these insulating films.

[0026]

The cleaning solution of the present invention

may be used singly, but may be used in admixture with other chemicals as far as the attainment of the present invention is not hindered.

As examples of other chemicals, mention may be made of various anionic, cationic and nonionic surface active agents, dispersing agents, corrosion inhibitors for metals, aqueous hydrogen peroxide, etc.

Moreover, anti-foaming agents may be added for inhibiting the foaming caused by the surface active agents.

The anti-foaming agents include, for example, anti-foaming agents of silicone type, polyether type, special nonionic type, fatty acid ester type, etc. and water-soluble organic compounds such as methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-1-propanol, acetone, and methyl ethyl ketone.

[0027]

20

25

The methods for cleaning semiconductor substrates (silicon wafer, etc.) using the cleaning solution of the present invention include, for example, a dip cleaning method which comprises directly dipping the wafer in the cleaning solution, a dip cleaning method which is combined with application of ultrasonic waves, a spray cleaning method which comprises spraying the cleaning solution onto the surface of the substrate, a brush scrubbing method which comprises cleaning by a brush while spraying the cleaning solution, a brush scrubbing method which is further combined with

application of ultrasonic waves, etc.

The cleaning solution may be heated for cleaning.

[0028]

As an example of cleaning with the cleaning solution of the present invention, explanation will be made of a case where a wafer on which an insulating film of low dielectric constant is exposed is cleaned in production of semiconductor devices.

10 First, as shown in FIG. 1(a), a silicon oxide film 1 and a silicon nitride film 2 are formed on a semiconductor substrate (not shown) on which elements such as transistor are formed, and thereafter an insulating film 3 of low dielectric constant and a cap layer film 4 (e.g., SiO_2 film) for protecting the 15 insulating film of low dielectric constant are formed. Then, a groove is formed by a known lithography process, and thereafter a barrier metal film 5 and a copper film 6 are formed as shown in FIG. 1(b), and a copper wiring is formed by polishing the copper film and the barrier 20 metal film using a known CMP process. Thereafter, the polishing detritus deposited on the surface by polishing, slurry components and metallic impurities in the polishing agent, etc. as shown in FIG. 1(c) are 25 removed. In case the CMP process can perform uniform polishing of the surface of the wafer, the insulating film of low dielectric constant is not exposed on the surface, but in case the polishing cannot be uniformly

carried out, a part of the cap layer is sometimes removed by the polishing to expose the insulating film of low dielectric constant as shown in FIG. 1(c-2). In this case, the exposed insulating film of low dielectric constant can hardly be cleaned by the conventional cleaning solutions, but the cleaning solution of the present invention can be applied to cleaning of the exposed insulating film.

Moreover, in the case of wide wiring, 10 desiccation is apt to occur, and when a cap layer film 7 is formed on the copper wiring and further an upper insulating film 8 of low dielectric constant is formed after completion of cleaning, a dent portion is also formed on the upper insulating film 8 of low dielectric 15 constant reflecting the dent portion at the center of the Cu wiring, thereby to make the film 8 uneven. the insulating film 8 of low dielectric constant has a dent portion, there may occur the possibility of being out of focus in the lithography of the subsequent step, 20 and hence the insulating film of low dielectric constant must be flattened by CMP process. The cleaning solution of the present invention can also be applied to removal of the foreign substances on the surface of such an insulating film after subjected to polishing by CMP 25 process.

[0029]

The cleaning solution of the present invention is excellent in removal of particulate foreign

substances and ionic foreign substances on semiconductor substrates after subjected to CMP process and can be suitably used for cleaning of the surface of the substrates on which an insulating film of low dielectric constant having hydrophobic surface is exposed.

[0030]

Examples

The present invention will be explained in more detail based on the following examples, which should not be construed as limiting the invention in any manner.

[0031]

Example 1

25

Composition of cleaning solution is shown in

15 Table 1. A wafer having an SiOC film which was a kind
of an insulating film of low dielectric constant, and
the surface of which was previously contaminated with
fine particles and metal impurities was cleaned using
the cleaning solutions and a brush cleaning apparatus.

20 The concentrations of the remaining fine particles and
metal impurities are also shown in Table 1.

The contamination of the surface of the SiOC film wafer with fine particles before cleaning was conducted by dipping the wafer in a slurry for CuCMP to contaminate the surface of the film with abrasive grains in the slurry. The number of contaminating particles before cleaning was 3000/wafer. The contamination with metal impurities was conducted by actually polishing the

Cu film by CuCMP to contaminate the exposed SiOC film with metals. The degree of contamination with metals before cleaning was 5×10^{12} atoms/cm² in the case of Cu.

[0032]

5 [Table 1]

	Example 1
EMULGEN 108 *1	0.1%
Ammonium oxalate	0.1%
Hydroxyethanediphosphonic acid	0.01%
NH ₄ OH	0.05%
NH ₄ F	0.4%
The number of fine particles after cleaning(number/wafer)	40
Amount of deposited Cu after cleaning (\times 10 ¹⁰ atoms/cm ²)	<1

*1: A nonionic surface active agent (1) wherein 1 is 11, m is 2, n is 8, and X is a hydrogen atom; Polyoxyethylene lauryl ether manufactured by Kao Co., Ltd.

10 [0033]

15

As shown in Table 1, fine particles and Cu impurities on the SiOC film were removed to such a level as necessary for production of semiconductor devices by washing with the cleaning solution of the present invention.

[0034]

Comparative Examples 1 and 2

The SiOC film contaminated with fine particles by the same method in Example 1 was cleaned using the

20 brush cleaning apparatus. The cleaning solutions were shown in Table 2 in which the surface active agents in the cleaning solutions were changed. The cleaning

solutions were compared on fine particle removability, and the results are shown in Table 2. Furthermore, wettability of each cleaning solution with SiOC film was compared by measuring the contact angle of the cleaning solution and the SiOC film.

[0035]

[Table 2]

	Example 1	Comparative Example 1	Comparative Example 2
EMULGEN 108	0.1%		
SOFUTANOL 70 *2		0.1%	
Ammonium oxalate	0.1%	0.1%	0.1%
Hydroxyethane- diphosphonic acid	0.01%	0.01%	0.01%
NH ₄ OH	0.05%	0.05%	0.05%
NH ₄ F	0.4%	0.4%	0.4%
The number of fine particles after cleaning (number/wafer)	40	500	3000
Contact angle with SiOC film (°)	28	30	89

*2: A secondary higher alcohol ethoxylate manufactured by NIPPON SHOKUBAI CO., LTD. A surface active agent (2) in which m is 2, n is 7, and X is a hydrogen atom and prepared using a secondary alcohol having an oleophilic group of 12 carbon atoms.

[0036]

As shown in Table 2, wettability with the SiOC film was inferior and fine particles were hardly removed in Comparative Example 2 where no surface active agent was contained. On the other hand, by adding the surface active agent, the wettability could be improved, but the surface active agent of Comparative Example 1 was

inferior in fine particle removability and was at such a level as insufficient for producing semiconductor devices.

[0037]

5 Comparative Examples 3 and 4

A silicon oxide film wafer was immersed for 2 minutes in the cleaning solutions shown in Table 3.

Thereafter the amount of metals remaining on the surface of the wafer was analyzed. Before cleaning, the silicon oxide film wafer was revolved on a spin coater revolving at 200 rpm, and 40 ml of ultrahigh purity water containing 1 ppm of Fe and Al was dripped on the surface to contaminate the surface of the silicon oxide film with metals. As to the amounts of metals deposited on the surface before cleaning, the amount of Fe was 490 x 10¹⁰ atoms/cm² and that of Al was 340 x 10¹⁰ atoms/cm².

[0038]

[Table 3]

	Example 1	Comparative Example 3	Comparative Example 4
EMULGEN 108	0.1%	0.1%	0.1%
Ammonium oxalate	0.1%	0.1%	
Hydroxyethane- diphosphonic acid	0.01%	0.01%	
NH ₄ OH	0.05%		
NH ₄ F	0.4%		
Amount of deposited Fe (x 10 ¹⁰ atoms/cm ²)	6	86	460
Amount of deposited Al (x 10 ¹⁰ atoms/cm ²)	9	320	330

[0039]

As can be seen from Table 3, the cleaning solution of Example 1 exhibited satisfactory metal removability while the cleaning solution of Comparative Example 4 containing no chelating agent and that of Comparative Example 3 containing no chelating accelerator had no sufficient metal removability.

[0040]

Examples 2 and Comparative Examples 5 and 6

10 Contact angles of the cleaning solutions 6-9 containing various surface active agents dissolved therein with low dielectric constant film were measured. The results are also shown in Table 4. Furthermore, the solubility of the surface active agents was evaluated by visual inspection of turbidity of the solutions. A PAE film was used as the low dielectric constant film, and the concentration of the surface active agent in the cleaning solutions was 0.1%.

[0041]

20 [Table 4]

	Example 2	Comparative Example 5	Comparative Example 6
Surface active Agent	EMULGEN 108	N-520 *3	EH-6 *4
Contact angle	28	. 67	51
Turbidity	No	No	Cloudy

*3: Polyoxyethylenenonylphenyl ether manufactured by AOKI OIL INDUSTRIAL CO., LTD., a surface active agent in which the oleophilic group of is nonylphenyl group, m is

2, n is 20, and X is a hydrogen atom.

*4: Polyoxyethylene 2-ethylhexyl ether manufactured by AOKI OIL INDUSTRIAL CO., LTD., a surface active agent in which the oleophilic group is 2-ethylhexyl group, m is 2, n is 6, and X is a hydrogen atom.

[0042]

As shown in Table 4, when the surface active agents similar to the surface active agent of the formula (1), but differing in the structure of the oleophilic group from the surface active agent of the formula (1) were used, the contact angle with the low dielectric constant film was great, and wettability was inferior, and, furthermore, the surface active agents did not dissolve in the cleaning solution and made the solution cloudy.

[0043]

[Effects of the Invention]

According to the present invention, there can be provided a cleaning solution excellent in

20 removability for particulate foreign substances and ionic foreign substances on the semiconductor substrate after subjected to CMP process.

[Brief Description of Drawings]

[FIG. 1] Sectional flow sheet which shows one example
25 of steps for producing a semiconductor device using the
cleaning solution of the present invention.

[Description of Reference Numerals]

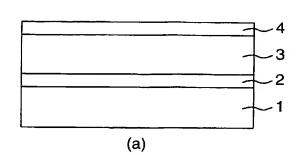
Silicon oxide film

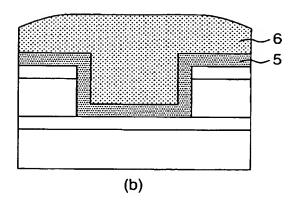
	2	Silicon nitride film
	3	Insulating film of low dielectric constant
	4	Cap layer film
	5	Barrier metal film
5	6	Copper film
	7	Cap layer film
	8	Insulating film of low dielectric constant

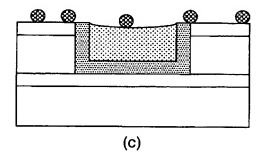
(Kind of Document) Drawing (FIG. 1)

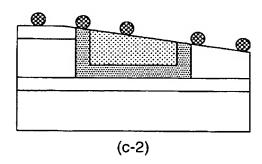


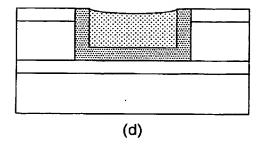
FIG. 1

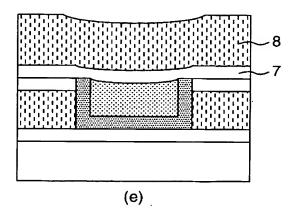


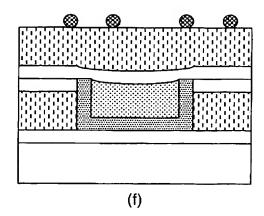












ON O T 2006 W

[Kind of Document] Abstract

[Abstract]

[Problem] To provide a cleaning solution excellent in removability for particulate foreign matters and ionic foreign matters on a semiconductor substrate after subjected to CMP process.

[Solution]

[1] A cleaning solution for semiconductor substrates comprising a nonionic surface active agent of the formula (1), a chelating agent and a chelating accelerator:

$$CH_3 - (CH_2)_1 - O - (C_m H_{2m}O)_n - X$$
 (1)

(wherein 1, m and n independently represent a positive number, and X represents a hydrogen atom or a hydrocarbon group)

[2] A cleaning solutin of [1] which additionally contains a conrrosion inhibitor for metals.

[Selected Drawing] No